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relana® Communication Note 21-01

Analysis of Pyridate according to the residue definition

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1. Introduction

The post-emergence herbicide Pyridate is often detected in several vegetables or at least in specific parts of vegetables like in celery leaves.
The residue definition (RD) includes not only the parent compound Pyridate but additionally its hydrolysis product Pyridafol (named CL 9673 in the RD) and hydrolysable conjugates of Pyridafol. Pyridate itself and free Pyridafol (not conjugated) are covered by the multi residue method QuEChERS. The aim of this project was to gain information about the proportion of the hydrolysable conjugates compared to free (non-conjugated) Pyridate and Pyridafol.

2. Analytical approach

The multi residue method QuEChERS is appropriate to detect and quantify Pyridate and Pyridafol while applying the common parameters and conditions described in the related literature [EN 15662, QUECHERS].

The hydrolysis approach applied is based on the commonly described procedures to determine the conjugates of acidic herbicides. This alkaline hydrolysis approach is published by Steinborn et.al. [STEINBORN] and is also described in the relana® position paper no. 16-05. The multi residue method EN 15662 includes this alkaline hydrolysis step as module E8 "*Extraction of 10g sample without addition of water with acetonitrile under simultaneous alkaline hydrolysis of base-labile esters and conjugates*". In the "brief description E8" it is mentioned: "*This extraction module is currently not applicable to conjugates of 6OH- and 8OH-Bentazone, Dicamba and Pyridate.*"

3. Comparison test celery leaves

The test material consists of celery leaves sent in by a customer of one participating relana® laboratory. The celery leaves were intended for putting them into the market, so they are a commonly produced food product with incurred residues of the applied pesticides during cultivation.
The test material was prepared by the laboratory receiving the sample as usual for routine samples. After chopping and homogenisation of the material, the resulting homogenate was analysed, and the remaining portion were stored frozen (-20°C).

After the first analysing laboratory evaluated the results with and without applying a hydrolysis step it became obvious, that the results related to Pyridate and its' hydrolysis products differ significantly depending on the applied methods. As a consequence, the laboratory informed relana® (Lach&Bruns) about its' observations and asked about interested laboratories to confirm the results.

After contacting several laboratories of the relana® circle, it was decided, to include two of them into this small comparison test. The remaining and frozen test material was subdivided into several portions and sent under frozen conditions to the 2 other relana® laboratories. They also analysed the test material with and without applying the hydrolysis step.

4. Results

The results of the 3 participating laboratories are summarised in the table below:

Results in µg/kg (ppb)	Lab 1	Lab 2	Lab 3
Time of analysis	12.11.2020	25.11.2020	26.11.2020
Pyridate	n.d. < 10	n.d. < 10	n.d. < 10
Pyridafol	15	90	78
Pyridate according to residue definition (appl. hydrolysis step)	198	220	183

5. Discussion

The levels of Pyridafol differ between lab 1 and the other labs 2 and 3, while the reported levels after applying the hydrolysis step are close together. This might be linked to the fact, that the results of lab 1 were obtained during the initial analyses after receiving the sample from the customer. Labs 2 and 3 received the samples with a delay of 2 weeks. Additionally, the retain samples were frozen, thawed, subdivided, frozen again, shipped, thawed again and then analysed. This might have affected the level of Pyridafol, as parts of the conjugates of Pyridafol might have been converted back to Pyridafol during these processes. This is supported by the fact, that the total level of Pyridafol and its' hydrolyses products is reported quite similar by all 3 laboratories.

6. Conclusion

The results of this small comparison test with celery leaves provide evidence, that it is essential to apply the hydrolysis to determine the correct level of Pyridate according to the residue definition. Without applying the hydrolysis, the total amount of the Pyridate hydrolysis product Pyridafol and its' conjugates will be covered to a significantly lower extent only. Therefore, it should be mandatory to re-analyse a sample by applying the hydrolysis step, even if only traces of Pyridafol are detected during the initial multi residue analysis.

Related to the hydrolysable conjugates of Pyridafol resp. Pyridate, the outcome of this comparison test is in contradiction to the statement in chapter E8 of the EN 15662, mentioning "*This extraction module is currently not applicable to conjugates of 6OH- and 8OH-Bentazone, Dicamba and Pyridate.*" This statement should be investigated in detail and critically reviewed if the observations made during this relana® comparative test can be confirmed.

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Participants of the comparison test:
Greit s.r.l., Bologna, Italy (Initiator of the project)
Labor Friedle GmbH, Tegernheim, Germany
PRIMORIS Belgium cvba, Zwijnaarde (Ghent), Belgium

References

EN 15662 „Foods of plant origin - Multimethod for the determination of pesticide residues using GC- and LC-based analysis following acetonitrile extraction/ partitioning and clean-up by dispersive SPE - Modular QuEChERS-method"

QUECHERS: https://www.quechers.com/index.php?nav1o=1&nav2o=0&nav3o=0

RELANA: relana® position paper no. 16-05, https://www.relana-online.de/wp-content/uploads/2016/08/PP_16-05_acidic-herbicides_vers20160808.pdf

STEINBORN: Angelika Steinborn, Lutz Alder, Madeleine Spitzke, Daniela Dörk, and Michelangelo Anastassiades „*Development of a QuEChERS-Based Method for the Simultaneous Determination of Acidic Pesticides, Their Esters, and Conjugates Following Alkaline Hydrolysis*", J.Agric.Food Chem. 2017, 65, 1296-1305

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